Supramolecular Chemistry

Outline

Lecture 8: Assembly of Materials using Hydrogen Bonding
Lecture 9: Assembly of Materials using Metal Ion Complexation
Lecture 10: Applications of New Materials

Overview of Last Week
Clathrates: Crystalline Host-Guest Systems

Limitations of the VDW/Hydrogen Bonding Approach to Clathrate Formation

- Only moderate control over the directionality of host-host interactions
  ⇒ limited “design” capabilities, with multiple structure types possible and only limited predictability of structure-property relationships
- Relative weakness of host-host interactions
  ⇒ moderate thermal and chemical stability, slight solubility
  ⇒ flexibility of lattice can limit size/shape selectivity
  ⇒ presence of strong host-guest interactions may have a dramatic influence on which structure-type will form

For many applications, more robust host lattices with better defined structures are required
  ⇒ need stronger, more directional bonds

Metal Ion Complexation in 2D Supramolecular Assembly
Metal Ion Complexation in 3D Supramolecular Assembly

<table>
<thead>
<tr>
<th>Bispidine &amp; Bidentate</th>
<th>50-90°</th>
<th>60°</th>
<th>180°</th>
</tr>
</thead>
<tbody>
<tr>
<td>60°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90°</td>
<td>triangle bi/tridentate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120°</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The same idea can be used to create extended frameworks

Molecular Framework Complexes

\[
\text{(Metal)}^{n+} + \text{Molecular Framework Complexes}
\]
Design and Construction (“Crystal Engineering”)

Diamond structure built from tetrahedral centres

Robson (1990) - expanded diamond-type frameworks using larger tetrahedral building units

Robson (1990) - generated the first family of compounds where it was possible to reliably predict the structures before the crystals were actually made.

\[ \text{Cu}^+ + [\text{Zn}^{II}(\text{CN})_4]^{2-} + \text{N}(	ext{CH}_3)_4^+ \]

Void regions within the lattice are filled with anions and solvent of crystallisation ⇒ opportunity for host-guest chemistry

The Hofmann Clathrates

Building Molecular Squares (1997)

Cyano-linkage through two cis-positions at 90°.
Capping of other sites.

Building Square Molecular Layers (1897) - the Hofmann Clathrates

Cyano-linkage through equatorial sites at 90°.
No capping required.

The Hofmann Clathrates: Structures

Strong interactions in 2D (to form rigid layers) but only weak interactions in the 3rd direction
⇒ 2D layers can stack on top of each other in many different ways

This structural flexibility is reflected in the host-guest chemistry, where it is seen that a number of different sizes and shapes of molecules may be accommodated into the voids.
The Hofmann Clathrates: Guest-Exchange Properties

- Despite the flexibility in the layer stacking, the guest-exchange properties of the Hofmann clathrates are greatly more predictable & consistent than those of the Werner clathrates.
  ⇒ the chromatographic properties show no significant dependence on sample history or on which guest molecules are included in the pores.
- Large lattice energy
  ⇒ very good thermal stability (>200 °C)
  ⇒ Purification of benzene and many other aromatics

The Hofmann Clathrates: Structural Variations

- Bridging of layers leads to the formation of 3D frameworks with improved rigidity and guest-exchange selectivity.
- Variable bridge-length ⇒ variable pores

The Prussian Blues

Building Molecular Cubes (1999)
Cyano-linkage through three cis-positions at 90°.
Capping of other sites.

Building Cubic Molecular Lattices (1710) - the Prussian Blues
Cyano-linkage through octahedral sites at 90°.
No capping required.
The Prussian Blues: Physical Properties

**Host-Guest Properties**
- First observation of permanent microporosity (retention of structure following removal of guests to leave voids) in an organic-based material, attributable to the rigid 3D structure. Micropores are only large enough to house very small guest molecules.

**Magnetic Properties**
- Highest temperature molecule-based magnets known, and the only room temperature magnets yet made that are optically transparent.

**Use of Larger Connecting Units:**
- **Extended Networks with 4,4’-Bipyridine**
  - Hofmann-type structures form with square planar coordination. Larger squares (~ 11 Å, cf. 5 Å for Hofmann) permits guest migration through the layers ⇒ increased rate of guest-exchange ⇒ better size-selectivity
  - The first observation of heterogeneous catalysis by a porous molecular solid (cyanosilation of aldehydes)

**Use of Larger Connecting Units:**
- **Extended Networks with Carboxy Ligands**
  - A large number of metal ion complexes of carboxy ligands are known, with a wide range of geometries. These can be linked together if multiply coordinating carboxy ligands are used.

**MOF-5: Prussian Blue-type Structure with Terephthalate (1,4-benzenedicarboxylate, bdc)**
- The \([\text{Zn}_4\text{O}(\text{O}_2\text{CR})_6]\) complex is an octahedral species with very high thermal stability.
  - Linkage of \([\text{Zn}_4\text{O}(\text{O}_2\text{CR})_6]\) centres through bdc “struts”
  - Microporous material with 19 Å cavities that is stable to 300 °C
**MOF-5: Microporosity**

Up-take and release of guest molecules is fully reversible. Microporous (removal of guests leaves lattice intact)

![Graph](image1.png)

<table>
<thead>
<tr>
<th>Surface</th>
<th>P (°C)</th>
<th>Amount adsorbed (mg/g)</th>
<th>Sorbate molecules per unit cell</th>
<th>Free volume (cm³/g)</th>
<th>Free volume (cm³/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>-194</td>
<td>1,460</td>
<td>280</td>
<td>1.02</td>
<td>0.01</td>
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<tr>
<td>N₂</td>
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<td>511</td>
<td>190</td>
<td>1.04</td>
<td>0.01</td>
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<td>CH₄</td>
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<tr>
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<td>71</td>
<td>0.94</td>
<td>0.05</td>
</tr>
<tr>
<td>CO</td>
<td>29</td>
<td>602</td>
<td>63</td>
<td>0.64</td>
<td>0.03</td>
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<tr>
<td>H₂O</td>
<td>29</td>
<td>1.472</td>
<td>59</td>
<td>0.94</td>
<td>0.05</td>
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<tr>
<td>CH₃OH</td>
<td>29</td>
<td>725</td>
<td>51</td>
<td>0.92</td>
<td>0.04</td>
</tr>
</tbody>
</table>

**Zn₃(btc)₂(OH)₃.x[guest]** (btc = 1,3,5-benzenetricarboxylate)

Square Planar + Triangular Connectors:

![Diagram](image2.png)

**POST-1: Chiral Framework Formation using Chiral Ligands**

![Diagram](image3.png)

**POST-1: Enantioselective Catalysis**

Transesterification of Esters

Replacement of EtOH with racemates of chiral alcohols leads to enantioselective catalyses to produce products with ee ~ 8%

![Graph](image4.png)